

Enhancing worker safety by minimizing health risks in hexavalent chromium environment

Effective Management of Hexavalent Chromium (Cr^{+6}) in DoD Organic and Inorganic Coatings Operations

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Sustaining Operations in Cr⁺⁶ Environment is Critical to DoD's Mission

- Battelle's dual approach focuses on;
 - Developing, evaluating, and deploying Cr⁺⁶ free materials and technologies, and in the interim,
 - Develop and recommend implementation of technologies to manage risks with Cr⁺⁶ usage during maintenance & overhaul of DoD assets

Organic Coatings

- Developed a non-Cr⁺⁶ corrosion inhibitor for use in primers
- HCR to eliminate Cr⁺⁶ release in the workplace during sustainment operations

Inorganic Coatings

- PCP to improve throughput and reduce waste from chrome plating operations
- Selective removal of dissolved metallic impurities to extend the life of chrome plating solutions

Eliminate Workplace Exposure, Improve Worker Safety, & Reduce Health Risks in Cr⁺⁶ Environment

ORGANIC COATINGS

Effectively Managing Hex Chrome Risks in DoD Sustainment Operations

1. Non-Chrome Primer as alternative to hex chrome
2. HCR to mitigate risks and safer workplaces

Non-Cr⁺⁶ Corrosion Inhibitor for Primer Coatings

- Battelle conducted an Internal Research & Development (IRAD) project to formulate a corrosion resistant primer coating using Ferrate (VI) metal compound as a replacement for hexavalent chromium
- Battelle tested performance of the corrosion resistant coating during a 5-year exposure test – **Coating formulations were not optimized**
- Primer tested IAW MIL-PRF-23377 approved epoxy primers
- Dry film thickness was as specified in Air Force Technical Order T.O 1-1-8
- No issues with HVLP spray application of admixed experimental primers



**Battelle's Ferrate (VI)
(K₂FeO₄)**

Ferrate (VI), a strong oxidizing agent has broad industrial applications including surface finishing. Battelle developed a technology for manufacturing high purity Ferrate (VI).

Technical Summary: Ferrate (VI) Primer Development

● Approach

■ Coating System Stack-ups (1 Scribed & 2 Unscribed)

- Set No. 1 (Control Primer, Topcoat)
- Set No. 2 (CCC, Control Primer, Topcoat)
- Set No. 3 (CCC, Barium Ferrate Primer, Topcoat)
- Set No. 4 (CCC, Strontium Ferrate Primer, Topcoat)
- Set No. 5 (NCCC, Control Primer, Topcoat)
- Set No. 6 (NCCC, Barium Ferrate Primer, Topcoat)
- Set No. 7 (NCCC, Strontium Ferrate Primer, Topcoat)

■ Coating Dry Film Thickness

- Primer (0.8 – 1.26 mil) Deft MIL-PRF23377D Type I Class N
- Topcoat (1.6 – 2.5 mil) – Deft MIL-PRF-85285D Type I Class H



Inspection Ranking Criteria

Scribe Corrosion Rating

- 0 Bright and clean
- 1 Staining no corrosion build up
- 2 Minor corrosion build up
- 3 Moderate corrosion build up
- 4 Major corrosion build up
- 5 Severe corrosion buildup

**Control Primer,
No Inhibitors
Rating: 5 – 3 – 4 – MD**



Scribe Blister/Undercutting Rating

- 0 No lifting of coating
- 1 Lifting or loss of adhesion up to 1/16" (2 mm)
- 2 Lifting or loss of adhesion up to 1/8" (3 mm)
- 3 Lifting or loss of adhesion up to 1/4" (6 mm)
- 4 Lifting or loss of adhesion up to 1/2" (13 mm)
- 5 Lifting or loss of adhesion beyond 1/2" (>13 mm)

Panel Blister Size

ASTM D 714

- 10 None
- 8 Very small
- 6 Small
- 4 Medium
- 2 Large

Blister Frequency

- | | |
|----|--------------|
| F | Few |
| M | Medium |
| MD | Medium Dense |
| D | Dense |

- All sprayed test panels were cured at 70 F and 50% RH for 14 days prior to exposure testing at the FMRF,
- Inspection intervals included; every quarter through 18 months, and then after 5 years
- Inspection criteria included a visual (10X magnification) examination of scribed and unscribed surfaces of control and experimental test panels,
- Close-up digital photographs document damage at critical intervals

Panel Exposure Results (5 years)

- Panels mounted at 30 degree incline and facing south for maximum UV exposure were at Battelle's FMRF for over 5 years
- Set 2 CCC, C Primer, Topcoat
- Set 4: CCC, SF Primer, Topcoat
- Dry Film Thickness
 - Primer (0.8 – 1.26 mil) Deft MIL-PRF-23377D Type I Class N
 - Topcoat (1.6 – 2.5 mil) – Deft MIL-PRF-85285D Type I Class H



Panel Exposure Results (5 years) cont'd

- Set 7: NCCC, SF Primer, Topcoat
- PreKote Pretreatment was applied to the test surfaces
- Dry Film Thickness
 - Primer (0.8 – 1.26 mil)
 - Topcoat (1.6 – 2.5 mil)
- All test panels were Al 2024-T3



Set 7

Ferrate (VI) Primer Development Results

- No problems were encountered during the preparation and application of the ferrate primers on bare Al2024-T3 coupons
- The chromated “control” stack-up performed as expected and should continue to offer superior corrosion protection to the scribed area
- Coupons with chromate conversion coating or chromate primer were consistent with results obtained on AFRL and NAVAIR PAX projects
- As measured by corrosion resistance and coating adhesion, Battelle’s ferrate primer performance was comparable to chromated primer when applied over a chromate conversion coating
- The Strontium Ferrate corrosion inhibitor performance was better than the primer system with Barium Ferrate in both scribed/unscribed condition
- The coating blisters noted along the edges of several test panels could have been reduced or eliminated with proper masking procedures

Sustaining Operations in Cr⁺⁶ Environment is Critical to DoD Mission

- Battelle funded an IRAD project to address the costly workplace Cr⁺⁶ exposure citations issued to AF and Navy Depots
- Our approach focused on efficient management of Cr⁺⁶ and eliminate its release into the workplace
- Hexavalent chromium reduction (HCR) technology, a chemical formulation **converting** the hazardous **Cr⁺⁶ to Cr⁺³ state**, before or at the point of release was developed
- OSHA does not regulate Cr⁺³ levels in workplace

HCR Eliminates Workplace Exposure, Improves Worker Safety, & Reduces Health Risks in Cr⁺⁶ Environment

HCR Technology Overview

- Product Formulation Components
 - Reducing agent (RA)
 - Carrying agent
 - Penetrating agent
 - CI package
- Application Methods
 - Spray
 - Immersion
 - Wipe
- Conversion Reaction



Applications

- Housekeeping

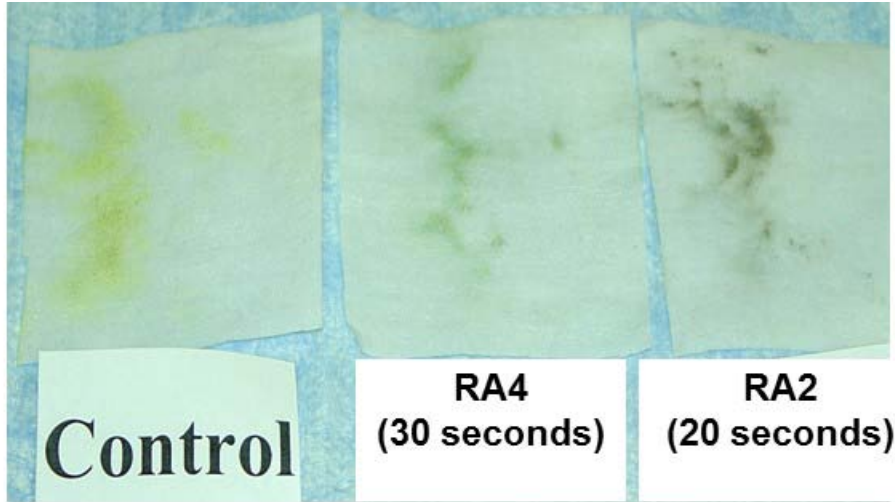
Aircraft Depainting



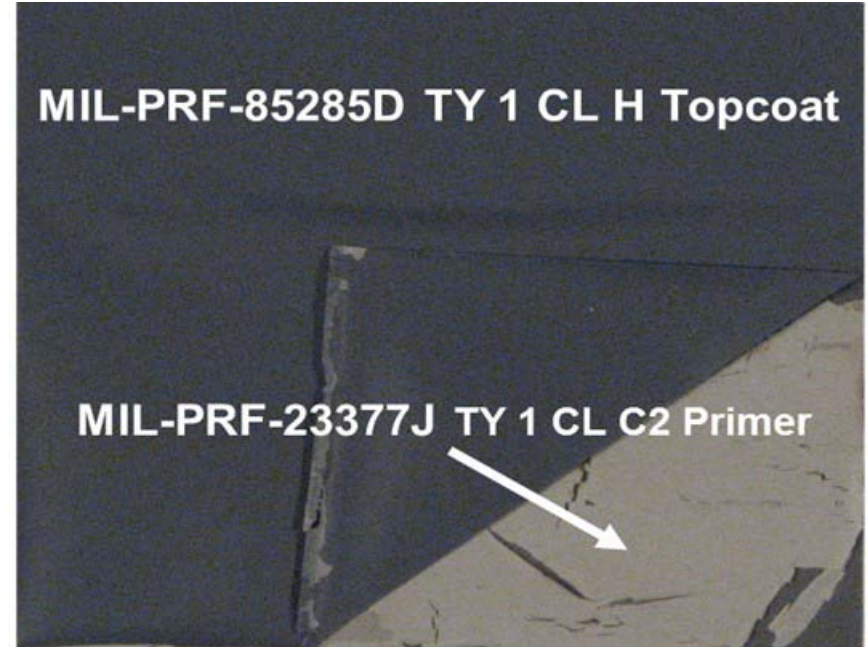
Wet Sanding



HCR Technology Performance



Demonstrated HCR on dry sanding of chromated primer and wipe application on contaminated surfaces



Topcoat delamination and complete reduction of Cr^{+6} to Cr^{+3} in MIL-SPEC primer on coupons saturated with HCR formulation

- HCR endorsement and support provided by SAF/IEE, ODASN/EI&E, and C-17 SPO
- U.S. Patent Pending Publication No. US2014/0223555 A1
- HCR materials compatibility testing funded by WR-ALC (March 2014)
- Proposed ALC and Multi-service Demonstration/Validation Testing (2015-2016)

WR-ALC Project Overview

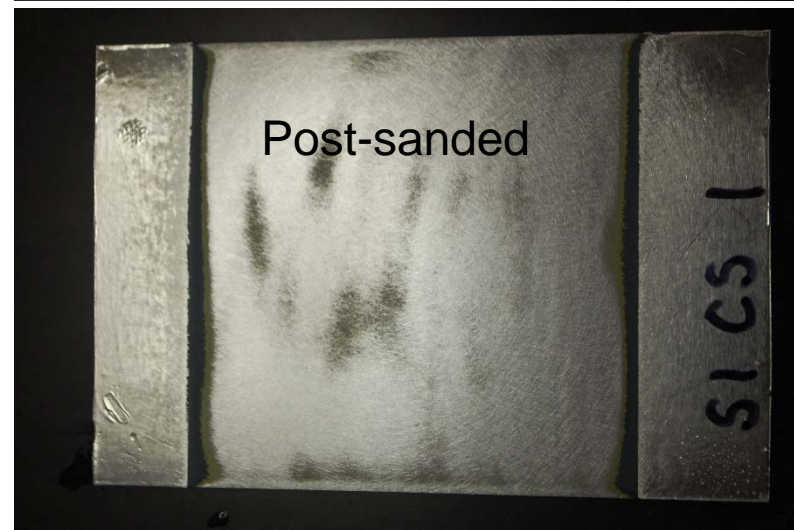
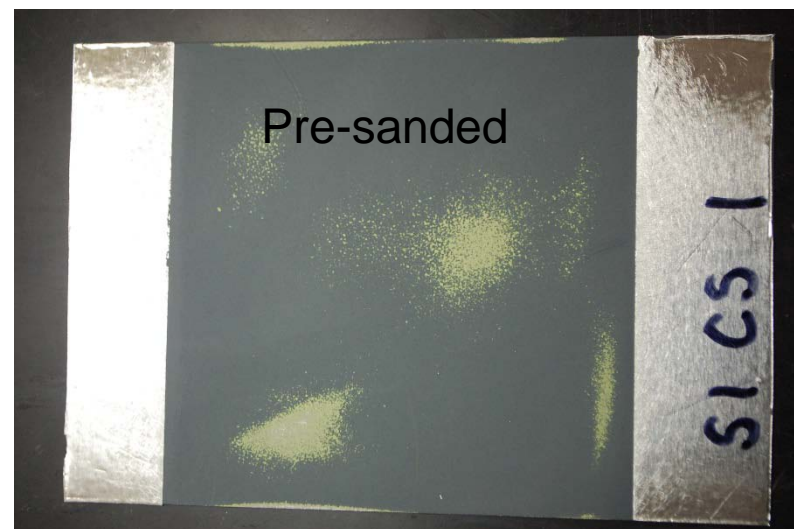
- Engineering qualification of the Cr^{+6} to Cr^{+3} reducing agent for wet sanding and housekeeping applications;
 - Performance:
 - Show that HCR reduces toxic Cr^{+6} to the OSHA non-regulated Cr^{+3} state
 - Material Compatibility:
 - Determine impacts of HCR on select aerospace substrates
 - ferrous (1020 CS and 4340 HSS), non-ferrous (Al 2024-T3, Al7075-T6, and Mg AZ31B-H24), and composites (Graphite-Epoxy, Fiberglass-Epoxy, and Kevlar)
 - Validation of Performance and Material Compatibility
 - External Tests: OSHA Method ID-215 for Cr^{+6} and for Type IV water dilutable heavy duty cleaning compound in accordance with MIL-PRF 87937D
 - Internal Tests: FTIR and SEM for compatibility with composites.

Technical Approach

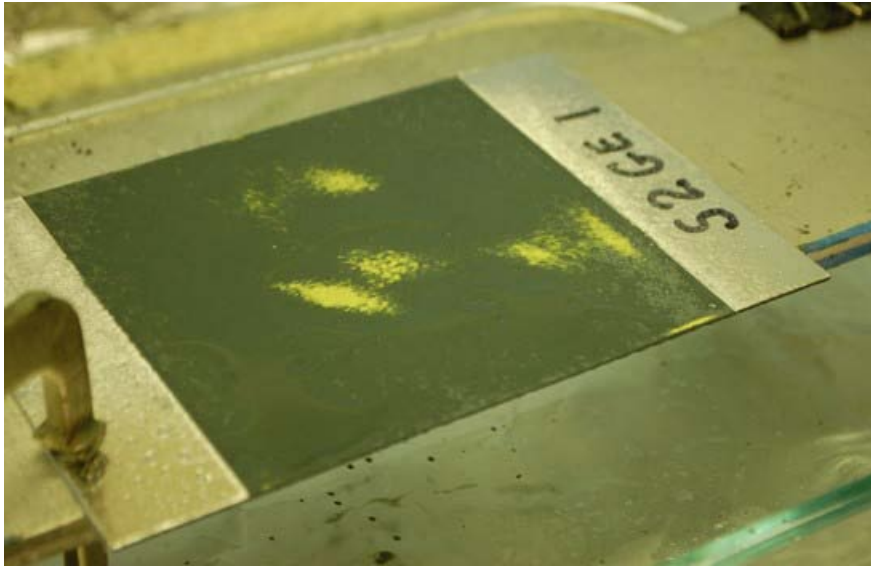
- Task 1: Develop Experimental Test Plan
- Task 2: Formulate HCR based on Battelle's IP
- Task 3: Prepare test panels with TO 1-1-8 approved coatings
 - MIL-PRF 23377J TY I CL C2 primer + MIL-PRF-85285E TY I CL H topcoat
 - Two dry film thicknesses of primer and single topcoat thickness were evaluated
- Task 4: Laboratory testing – at SMI Labs, Galson Labs, and Battelle
 - SMI for material compatibility on metals in accordance with MIL-C-87937D for Type IV heavy duty cleaning compound
 - Galson Labs for performance confirmation – Cr⁶ to Cr³ reduction
 - Battelle for FTIR and SEM characterization – material compatibility on three types of composites.
- Task 5: Results and data analysis
- Task 6 Develop and submit report

Wet Sanding Application

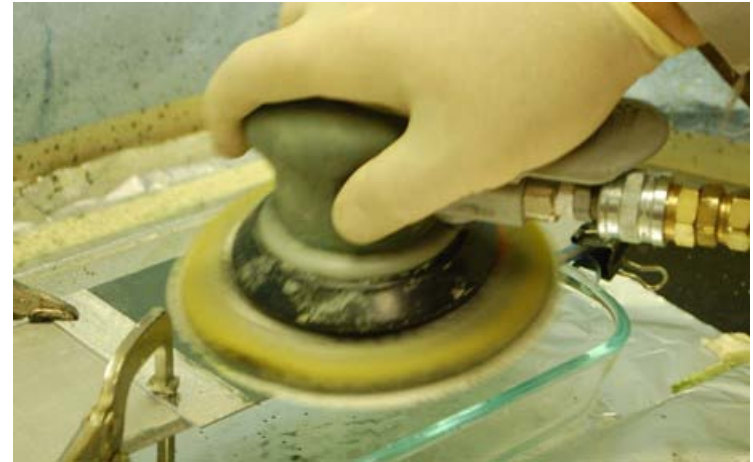
- Galson validated that MIL-SPEC topcoat does not compromise Cr^{+6} reduction process & efficiency
- Wet sanding with orbital sander and manual spray application of HCR solution
- Galson confirmed OSHA Method ID-215 analysis using dried powder analysis



Wet Sanding Application (cont'd....)



Spray application of HCR solution
(<30 second dwell time)



Sanding operation (1-2 minutes)



Visual confirmation of reduction

Wet Sanding Application Results

- Galson Laboratories Test results showing Cr⁶⁺ to Cr³⁺ reductions at expected levels
- Results are for composite samples of three separate wet sanding tests performed on separate coupons

Wet Sanding Application Performance						
Coupons with Single Dry Film Thickness						
Sample	Lab	Weight (g)	Total (µg)	Conc (mg/kg)	Untreated Conc (mg/kg)	Cr ⁶ to Cr ³ Reduction
SET 1	1010	0.071	0.48	6.7	12100	99.94%
SET 1	4340	0.1	5.6	55	12100	99.55%
SET 1	2024	0.1	0.77	7.5	12100	99.94%
SET 1	7075	0.1	1.4	13	12100	99.89%
SET 1	AZ31B	0.1	20	200	12100	98.35%
SET 1	Fiber Glass	0.1	0.033	0.33	12100	100.00%
SET 1	Graphite Epoxy	0.1	6	59	12100	99.51%
SET 1	Kevlar	0.1	3	29	12100	99.76%
Coupons with Double Dry Film Thickness						
Sample	Lab	Weight (g)	Total (µg)	Conc (mg/kg)	Untreated Conc (mg/kg)	Cr ⁶ to Cr ³ Reduction
SET 2	1010	0.1	360	3500	18900	81.48%
SET 2	4340	0.1	6.3	63	18900	99.67%
SET 2	2024	0.1	3.6	36	18900	99.81%
SET 2	7075	0.1	57	560	18900	97.04%
SET 2	AZ31B	0.1	380	3800	18900	79.89%
SET 2	FG	0.1	88	880	18900	95.34%
SET 2	GE	0.1	45	450	18900	97.62%
SET 2	K	0.1	4.7	46	18900	99.76%

Housekeeping Application

- Approximately 0.02 grams of Cr^{+6} primer powder applied to substrate surfaces
- HCR solution spray applied and allowed to dwell for 20-30 seconds before being wiped with dry PVC filter
- Collection filters allowed to air dry in labeled glass sample jars
- Jars sealed and sent to Galson Labs for analysis (residence time prior to analysis was 2 days)

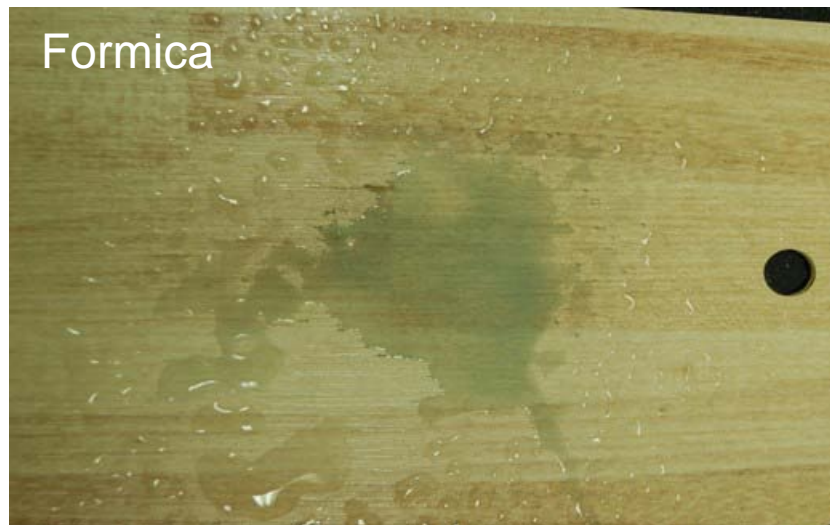
Control



Treated



Housekeeping Applications (cont'd)



Housekeeping Results

- Single HCR formulation used for validation testing of all substrates
- Test results confirm Cr⁶⁺ to Cr³⁺ reductions at expected levels
- Additional dwell time and saturated cloth wipes expected to increase efficiency and level of reduction

Housekeeping Application Performance (Primer Only) (Test 2)				
Sample	Sample	Total Cr ⁶⁺ (µg)	Cr ⁶⁺ to Cr ³⁺ Reduction	Average Cr ⁶⁺ to Cr ³⁺ Reduction
CONCRETE	CTR-CONCRETE A	86	N.A.	97.29%
	CONCRETE A	3.1	96.40%	
	CONCRETE B	1.7	98.02%	
	CONCRETE C	2.2	97.44%	
STEEL	CTR-STEEL A	39	N.A.	87.30%
	STEEL A	3.2	91.79%	
	STEEL B	0.66	98.31%	
	STEEL C	11	71.79%	
COATED STEEL	CTR-COATED STEEL A	120	N.A.	98.41%
	COATED STEEL A	0.92	99.23%	
	COATED STEEL B	2.6	97.83%	
	COATED STEEL C	2.2	98.17%	
WOOD	CTR-WOOD A	53	N.A.	96.79%
	WOOD A	1.2	97.74%	
	WOOD B	1.4	97.36%	
	WOOD C	2.5	95.28%	

Materials Compatibility Test Matrix



FTIR & SEM Conclusions

- All panel ATR spectra are dominated by epoxy resin
- All panel residue spectra are very weak indicating very little to no HCR residues remaining on panels
- No residue spectra indicate the presence of HCR on any panel type
- Spectra that do indicate residues are likely only due to epoxy-related materials/absorption bands
- SEM characterizations confirmed no “post-contact” residues on surfaces of composite panels

Three Pronged Tech Dev & Commercialization Strategy

Understand DoD challenges and establish HCR Technology merit

Work with stakeholders and evaluators such as NIOSH, Bioenvironmental, industrial hygienist and OSHA to acquire buy-in

Identify potential commercial partners to introduce HCR formulation into the DoD supply chain.

Develop & deploy HCR as an effective strategy to sustain DoD mission in Cr⁺⁶ environment

- *Eliminate Workplace Exposure to Cr⁺⁶*
- *Improve Worker Safety*
- *Reduce health risks in Cr⁺⁶ work environment*
- *Reduce worker's compensation expenses*

INORGANIC COATINGS

Effectively Managing Hex Chrome Risks in DOD Sustainment Operations – Primarily Electrolytic Hard Chrome (EHC) Plating

1. Precision Chrome Plating to Improve Throughput and Reduce Waste
2. Extending Chrome Plating Solution Life by Selective Removal of Dissolved Metallic Impurities

Precision Chrome Plating (PCP)

- PCP is a Battelle-developed integrated technology package for inorganic surface finishing process resulting in;
 - Increased productivity, reduced waste, and improved energy and environmental profile
 - Increased speed and uniformity = improved quality and optimized resource utilization
- PCP introduces a step-change to the plating process by integrating the following elements to deliver a consistent and uniform plating quality;
 - Plating Control System (PCS) for process automation and control
 - Innovative & Customized Tooling
 - Process chemistry and plating recipes
 - Onsite personnel training

Integrated Elements of PCP

Conforming anodes & fixtures, Efficient and programmable rectifiers / power supplies, In-tank filtration, Level and flow controls, Efficient / closed loop rinse system, efficient scrubbing system

Innovative & Customized Tooling

Personnel: Plating recipes and plating procedures, tips for faster and consistent plating quality

Onsite Personnel Training

PCP

Plating Control System

Custom-designed automation and plating performance management system with dedicated recipes, controls plating, monitors bath environment, generates reports, and serves as a database repository.

Process Chemistry & Plating Recipes

Optimized anode to cathode ratios, tank temperatures and operating conditions, Cr to SO₄ ratios, Custom plating recipes for PCP

Dramatic Process Improvements Drive Energy & Environmental Benefits

Automated PCS in the Plating Shop & Screen Shots

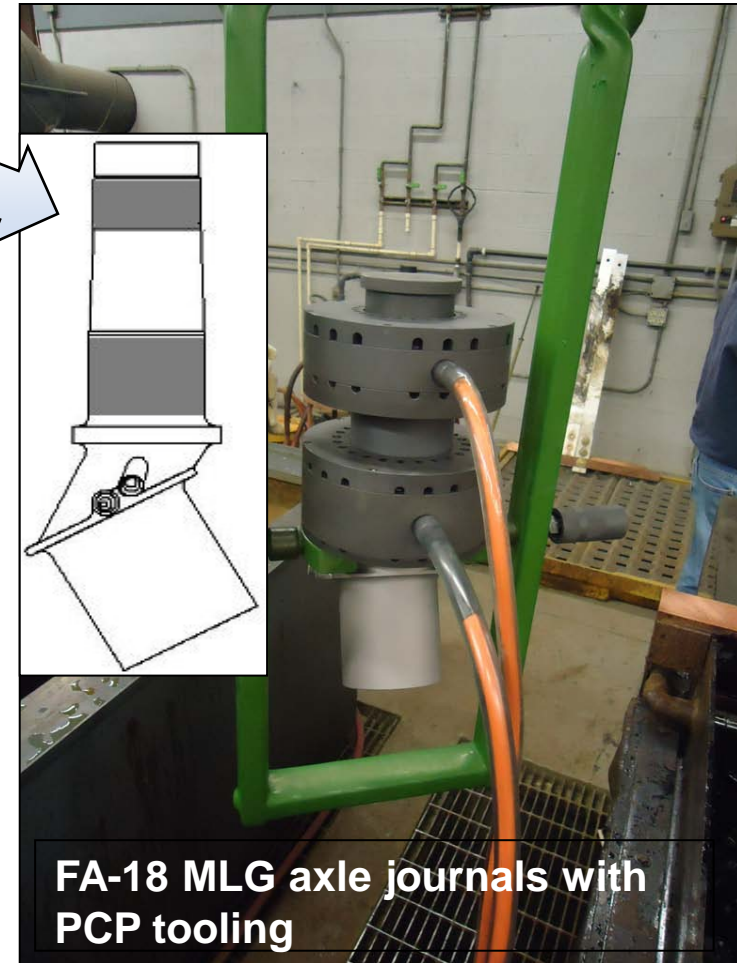
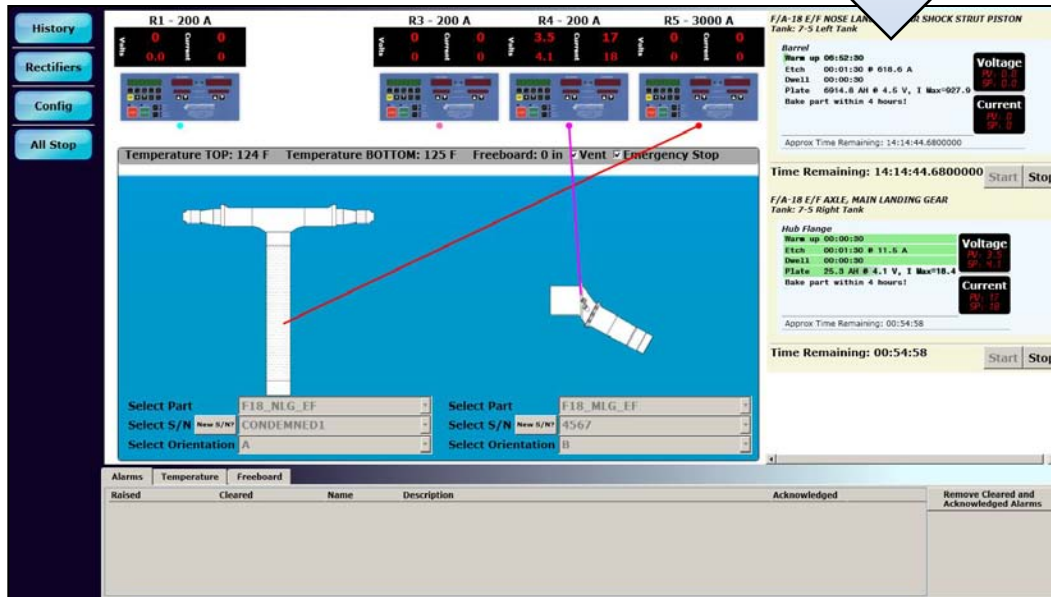
PCS installed in the chrome plating shop at FRCSW with Setup and Control screen shots for E2 Trunnion Pin (2578177)



FA-18 PCP Case Study

Custom tooling for the two shaded journals on the FA-18 MLG axle

PCS user interface showing two simultaneous plating cycles in the same tank (7-5) for FA-18 NLG piston and MLG axle



8 aircraft components with 21 regions and 2 chrome plating tanks transitioned to PCP at FRCSSW

PCP Case Study – E-2 Rotodome Shaft

- With 47% time savings (129 hours to 68 hours) productivity almost doubled (90%) with the same resources. **Note:** If a few other constraints are removed, additional gains could be realized.

Plating Step	Baseline Process	PCP Cycle Time	Time Savings
Masking / Setup	2 hours	0.5hours	1.5 hours; (75%)
Plating	70 hours	32 hours	38 hours; (54%)
De-masking / breakdown	1 hours	0.5 hours	0.5 hour; (50%)
Post Plate grinding	48 – 64 hours (56 avg)	29-39 hours (34 avg)	18 hours (avg) (40%)
Hazardous waste		Reduced by over 90%	
Energy usage	Not calculated	Significant energy savings from reduced timing for plating, and post-plate grinding	
Plating uniformity	According to platers and grinders, they have never been able to get such uniform plating. Eliminated requirement for excess plating thereby reducing hazardous waste from post-plate grinding operations		



Other PCP Time Savings Examples

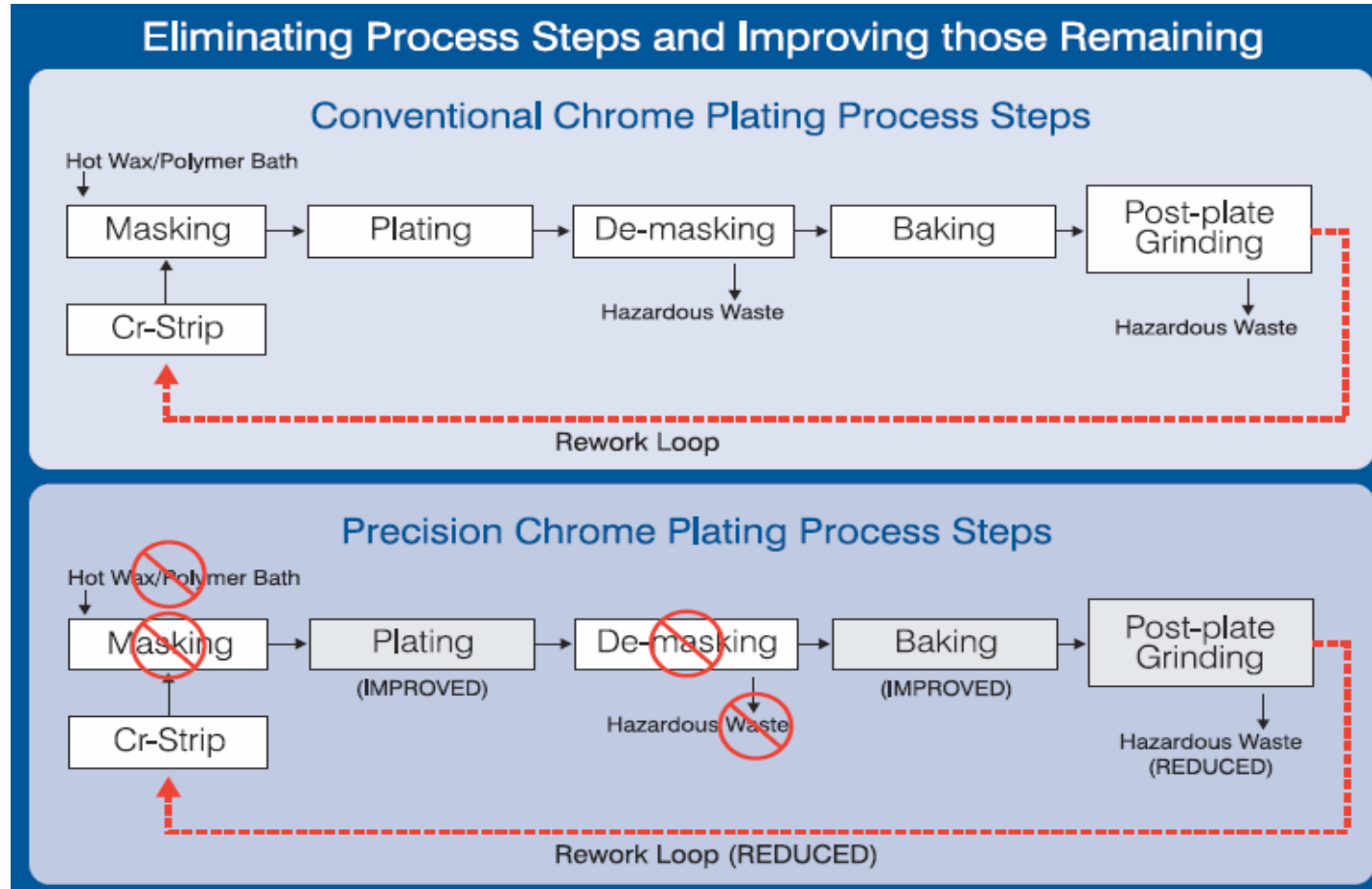
Aircraft Component (P/N)	Number of Regions	Plating Cycle Time* (Hrs.)	PCP Plating cycle Time* (Hrs.)	Time Savings Per Plating Cycle (Hrs.)	Time Savings Per Plating Cycle (%)
E2 Upper Torque Pin (2578197)	Two regions	29**	4.5	24.5	84
E2 Trunnion Pin (2578177)	Two regions	36	11	25	69
F18 Main Ram Actuator Piston (303247)	One region	39	6	33	85
F18 NLG cylinder (74A450602)	One region	48**	12.4	35.6	74
E2 Rotodome Shaft (123BM52104)	One region	129	68	61	47

* Plating Cycle Time includes; Time for Masking/Setup, Plating, Demasking, and Postplate grinding time.

** Estimated from discussions with platers because baseline plating logs for these parts were not available.

- PCP improves productivity because of accuracy and speed.
 - Accuracy (uniformity and concentricity) allows the platers to limit excess build of chrome thickness for post plate grinding.
 - Speed reduces the plating cycle time. Uniformity also reduces post-plate grinding time.
- For parts transitioned to PCP, FRCSW can more than double the annual production generating new revenue.

How does Integrated PCP Work?



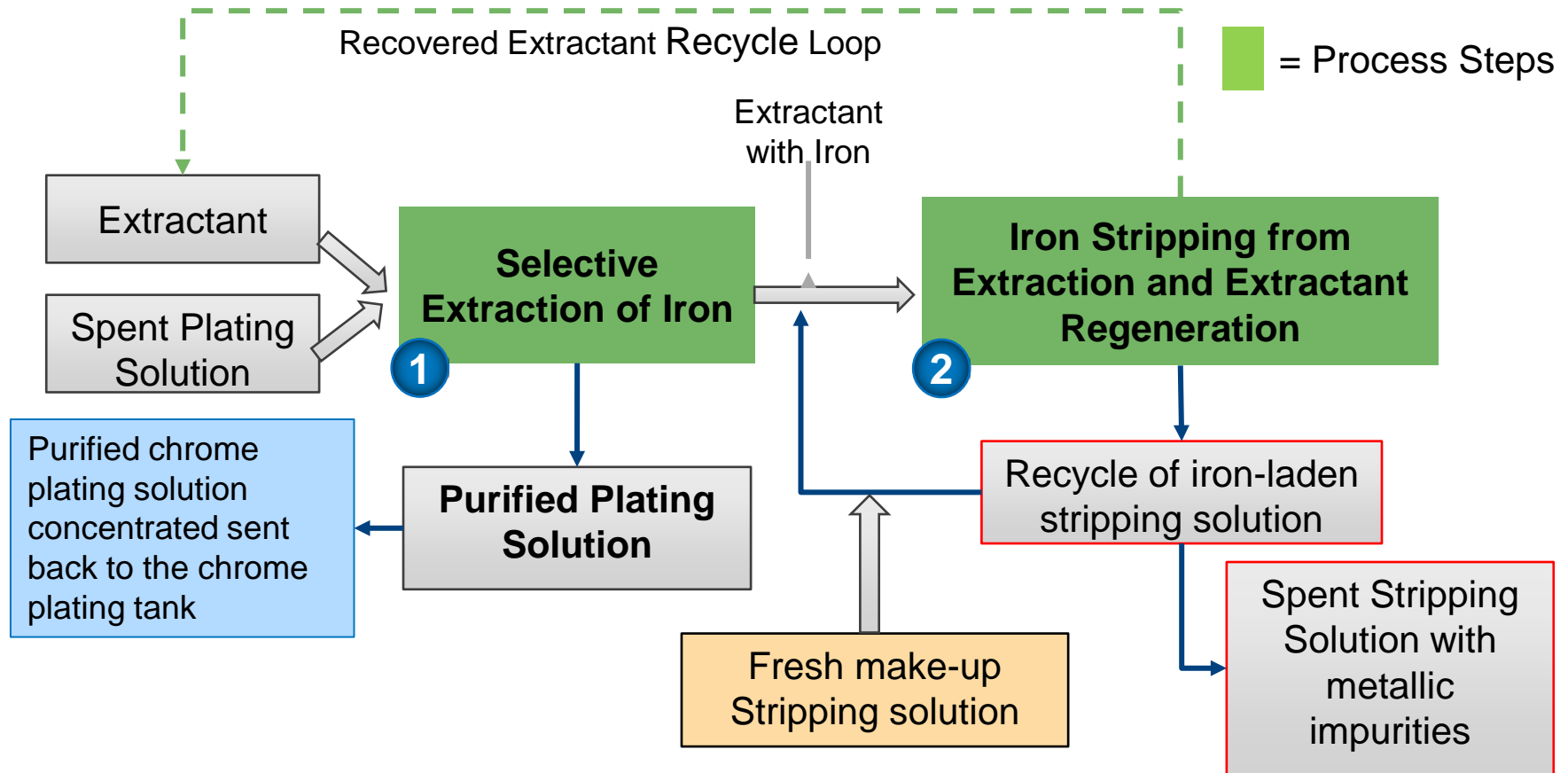
PCP produces uniform plating quality in significantly less time while eliminating multiple process steps

Extending Life of Chrome Plating Bath Solution (CPS)

- Dissolved metallic impurities like copper and iron severely affect the plating speed and quality.
- Bath chemistry is critical to the process performance and it is maintained by increasing chrome concentration in the tank
- Plating baths with high dissolved metal impurities are rejuvenated by partial disposal of the spent solutions and replacing it with fresh solutions.
- Disposal of spent chrome plating baths and makeup are a significant financial and environmental burden as the liability for the disposed spent solution remains with the generator.

Battelle applied its IP to develop a process that cost effectively extends life of the chrome plating solutions

CPS Purification Process Overview



- **1,000 gal CPS tank accumulating 0.01 g/l of iron (Fe) per day can be maintained in \$/day.**
- **Costs \$\$ to remove 1 gm/l of Fe in 1,000 L of CPS**